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The Friedel Crafts Reaction of  
Ethylene with Pentaborane-9

I. Dunstan

J. V. Griffiths

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## 1. SUMMARY

A review of the known alkyl derivatives of pentaborane-9 is presented.

A stainless steel autoclave has been used to study the reaction of ethylene with pentaborane in the presence of aluminium chloride catalyst. Attention has been given to the effect of temperature, catalyst ratio and ethylene pressure.

The separation of ethyl pentaborane from pentaborane has been achieved by fractional distillation under a small positive pressure of nitrogen.

Relative rates of hydrolysis of decaborane, ethyl decaborane and ethyl pentaborane have been measured in a dioxane/hydrochloric acid medium.

The preparation, purification and properties of ethyl pentaborane are discussed and comparison is made with ethyl decaborane.

## 2. INTRODUCTION

An earlier report (1) mentioned some of the reasons for current interest in the possibility of using compounds of boron, carbon and hydrogen as high energy fuels in aircraft engines. Alkyl derivatives of pentaborane and decaborane have attracted particular attention in this respect and it has been shown that these compounds may be prepared by Friedel Crafts reactions between the borane and a suitable alkylating agent in the presence of aluminium chloride as catalyst.

Under the conditions of the Friedel Crafts reaction decaborane underwent polysubstitution and derivatives containing up to four alkyl groups were isolated and characterised. Similar reaction products have been obtained in the U.S.A. (2, 3). Thus Hef-3, a boron fuel commercially available in the U.S.A., consists of decaborane (6.8 per cent), monoethyl (69.4 per cent), diethyl (22.4 per cent) and triethyl decaborane (1.4 per cent) (4, 5). HiCal-3, another boron fuel from a commercial source in America, prepared by simultaneous ethylation and pyrolysis of diborane and ethylene (6), contains mono and polyethylated decaborane as well as the corresponding derivatives of pentaborane (7, 8).

Introduction of alkyl groups into boranes, necessary if the product is to possess the physical properties required of a fuel, adversely affects the heat of combustion of the material, the effect increasing with number of substituents (9). It was of interest therefore, to observe that Friedel Crafts ethylation of pentaborane-9 with ethylene/aluminium chloride gave only monoethyl pentaborane and there was no evidence of polysubstitution (1, 10). The discovery encouraged further research to determine optimum conditions for the synthesis of ethyl pentaborane and the investigation forms the subject of this report.

/3. ....



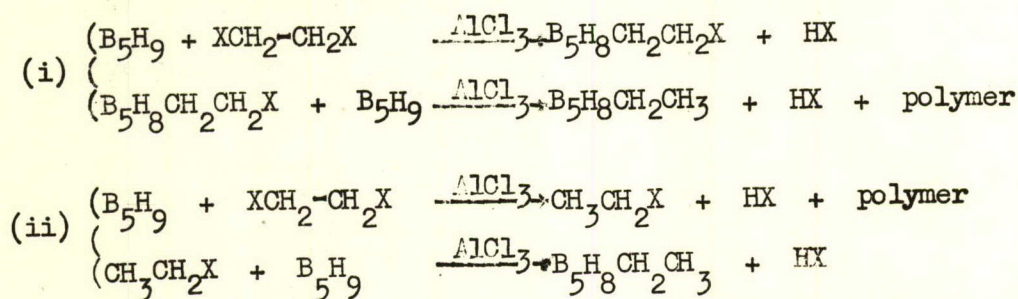
### 3. ALKYL DERIVATIVES OF PENTABORANE-9

The known, well-characterised derivatives of pentaborane-9 are listed in Table 1 (p.3). Aluminium chloride catalysed Friedel Crafts reactions have generally been used to prepare these compounds although several methyl derivatives were obtained by simultaneous pyrolysis and alkylation using boron trimethyl (14). A particularly interesting outcome of this work was the isolation of two isomeric monomethyl pentaboranes. One of the isomers, vapour pressure 35 mm.Hg/0°C, was identical with the apically substituted product obtained by Friedel Crafts methylation of pentaborane (1, 10).

Propyl pentaborane is the major constituent (70 - 85 per cent) of an American boron fuel, Hef-2 (6, 20). The material also contains dipropyl pentaborane (15 - 25 per cent) and pentaborane (3 - 5 per cent).

Gas chromatographic examination of HiCal-3 demonstrated the presence of small quantities of polyethylated pentaborane corresponding to diethyl (1.1 per cent), triethyl (3.2 per cent), tetra-ethyl (4.9 per cent) and penta-ethyl pentaborane (0.7 per cent) (7). These compounds were not sufficiently well-characterised for inclusion in the table.

Formation of ethyl pentaborane by reaction of pentaborane with 1,2-dibromoethane or 1,2-dichloroethane was to some extent unexpected (11). Two possible mechanisms were suggested to explain why these reactions should give ethyl pentaborane instead of the desired dipentaboranylethane. Reduction by pentaborane is involved in either process:



where X = Br or Cl.

Blundell (16) studied the Friedel Crafts alkylation of pentaborane with ethylene/aluminium chloride in a heated Nimonic autoclave and recorded yields of 20 to 35 per cent at 50°C with an ethylene pressure of 80 p.s.i.

In a parallel but independent investigation by the present authors efforts were made to obtain high yields of ethyl pentaborane accompanied by little or no side-product formation or loss of boron. Preliminary experiments, performed in sealed glass vessels, have been reported elsewhere (1); yields of the order of 40 per cent were obtained. This was followed up by work in a metal vessel, the results of which are now reported.

### 4. FRIEDEL CRAFTS ETHYLATION OF PENTABORANE-9

A 750 c.c. stainless steel autoclave was used to study the Friedel Crafts alkylation of pentaborane-9 with ethylene in the presence of aluminium chloride as catalyst. Experiments were conducted at various

/TABLE 1 .....



TABLE 1

## Alkyl Derivatives of Pentaborane-9

Formula	Preparation			Melting Point, °C	Vapour Pressure, mm. Hg.	Remarks	Bibliography Reference
	Reagent	Catalyst	Conditions	Yield, %			
$B_5H_8-CH_2-B_5H_8$	$CH_2Cl_2$	$AlCl_3$	$n-C_7H_{16}$ , Reflux, 5 h	0.36	51.5-53	-	11
$B_5H_8Me$					-	Probably apically substituted	12, 13, 14
$B_5H_8Me$					-63	Purified by gas chromatography	14
$B_5H_7Me_2$					-	Impure sample	14
$B_5H_6Me_3$					-	Impure sample	14
$B_5H_8Et$					-		13, 15
	$Cl-CH_2-CH_2-Cl$	$AlCl_3$	(i) Room temperature (ii) Reflux, 6 h.	20	13/0°C; 40/25°C; 760/104°C	-	11
	$Br-CH_2-CH_2-Br$	$AlCl_3$	$n-C_{10}H_{22}$ (i) Room temperature (ii) Reflux, 7 h.	47	15/0°C; 35/25°C	-	11
	$C_2H_4$	$AlCl_3$	50°C, 5 h.	34	11.8/0°C; 57/30.3°C; 760/103.5°C	-	16
	$C_2H_4$	$AlCl_3$	60°C, 5 h.	43	29/19.5°C	apically substituted	1, 10
$B_5H_8Pr$	-	-	-	-	-	-	17
$B_5H_8CH_2CH_2-SiCl_3$	$CH_2=CH-SiCl_3$	$AlCl_3$	(i) Room temperature (ii) 100°C, 17 h.	40	-	-	13
$(B_5H_8CH_2CH_2)_2SiCl_2$	$(ClCH_2CH_2)_2SiCl_2$	$AlCl_3$	Room temperature	-	-	Impure liquid	19

/temperatures .....



temperatures (room temperature to 70°C) and pressure of ethylene (5 to 112 p.s.i.g.) for periods of time ranging from 1 to 114 hours. Some attention was given to the effect of changing the mole ratio of catalyst to pentaborane. In each case the product was weighed and its per cent composition determined by gas chromatography.

It was not possible to carry out a complete systematic search for optimum conditions due to the limited availability of pentaborane. For this reason experiments were restricted to a 2 g. scale; altogether, 50 g. of pentaborane were consumed.

#### 4.1 Apparatus

The stainless steel reaction vessel used in these experiments is shown in Figure 1. Two valves and a pressure gauge (-30 inches Hg to 300 p.s.i.) of the same material were fitted to the lid which could be bolted to the body of the autoclave by a flange with a Teflon seating. A thermometer pocket was provided in the lid of the autoclave. Connections were made to a supply of ethylene from a cylinder and to a conventional vacuum line consisting of four fractionation traps, standard gas-measuring flasks (5 l., 1 l., 500 c.c., 250 c.c.), manometer, dry-nitrogen inlet and standard joints for the introduction or removal of material from the line. Pentaborane and ethyl pentaborane were stored in 1-litre stainless steel cylinders attached to the line by flexible stainless steel tubing brazed to brass standard joints.

The apparatus was entirely enclosed in an exhaust-ventilated cubicle equipped with sliding Perspex windows and externally-controlled services. A table situated below the autoclave carried heating and cooling baths; it could be raised or lowered from outside the cubicle.

#### 4.2 Method

In a typical experiment finely-powdered aluminium chloride was placed in the autoclave which had previously been flushed with dry nitrogen. The autoclave was assembled, evacuated and cooled in a solid-carbon-dioxide/acetone bath. Pentaborane, measured as gas, was distilled into the autoclave, which was closed and allowed to warm to room temperature (the temperature of the cubicle was thermostatically controlled in the range 25° ± 3°C). Ethylene was admitted to the desired pressure (Note (i)) and heating, if required, was commenced. Although the oil-bath was preheated to the desired temperature there was a time-lag of about an hour before the autoclave reached maximum temperature (Figure 2). After the appropriate reaction time, the autoclave was cooled (Note (ii)) and opened to the vacuum line through two traps cooled at -78.5°C and two liquid-nitrogen-cooled traps (Note (iii)). The product, which collected in the first two traps, was transferred by distillation to a weighing tube and then to a sampling trap (1). The latter was fitted with a serum cap through which samples could be withdrawn in a hypodermic syringe for subsequent analysis by gas chromatography.

Gas chromatographic analyses were performed in a Griffin and George Mk II apparatus using a column (2 m. x 5 mm. i.d.) packed with Apiezon L grease (20 per cent) supported on Embacel (80 per cent); hydrogen (5.8 l/h.) was used as carrier gas. The column and katharometer detector were maintained at a temperature of 60°C (10). A typical chromatogram is reproduced in Figure 3 to indicate the relative retention volumes of pentaborane, ethyl pentaborane and impurity.

/Analysis .....



Analysis of a mixture of pentaborane/ethyl pentaborane (1:2) of known composition showed that it was necessary to correct the area of the peak due to ethyl pentaborane by a calibration factor of 1.10.

Note (i) The exact volume of the autoclave was determined to be 768.1 c.c. Assuming ideal gas behaviour it was possible to calculate the number of moles of ethylene ( $M$ ) in the autoclave at a gauge pressure,  $P$  p.s.i.g., and at a temperature  $T^{\circ}K$ :

$$M = \frac{1}{T} (9.3612 + 0.637P)$$

By taking  $25^{\circ}C$  as ambient temperature the number of moles of ethylene used in a reaction was calculated from the equation:

$$M = 0.03142 + 0.002137P$$

where  $P$  is the initial pressure in p.s.i.g. (the contribution of pentaborane to this pressure has been ignored).

Note (ii) During early experiments under high ethylene pressures, decreases of pressure of 5 to 30 p.s.i. were observed. These changes have not been recorded in detail because it was impossible to read the pressure gauge with sufficient accuracy. It was important to use a small gauge to reduce dead space and consequently each scale division covered a pressure range of 10 p.s.i.

Note (iii) In later experiments involving smaller quantities of ethylene, the gas was measured volumetrically before and after each reaction (see Table 5). Ethylene was transferred to the autoclave by cooling with liquid nitrogen instead of with solid-carbon-dioxide/acetone.

#### 4.3 Effect of Temperature

The experiments listed in Table 2 are selected primarily to illustrate the effect of temperature on the ethylation of pentaborane. Other variables which clearly affect the yield of ethyl pentaborane are pressure and reaction time. The reactions fall conveniently into two groups - the low yields associated with high pressure (experiments 1 to 4) and the higher yields obtained at low pressures (experiments 9 to 12). The effect of temperature at low pressures of ethylene was demonstrated by the increase in yield which accompanied a decrease of temperature (experiments 9 to 12). A high reaction temperature not only resulted in low yields but also led to increased boron loss compared with the loss accompanying a room temperature reaction.

#### 4.4 Effect of Catalyst Ratio

Experiments in which larger catalyst:pentaborane ratios were used are summarised in Table 3. Both at room temperature and at  $60^{\circ}C$  reaction proceeded with much loss of boron-containing material. The reason for this loss was not determined but it seems likely that it might be explained by complex formation with the catalyst or by condensation under its influence.

An attempt to re-cycle the catalyst from experiment 19 (Table 4) resulted in a very poor conversion of pentaborane (experiment 20).

/TABLE 2 .....



TABLE 2

Effect of Temperature on the Ethylation of Pentaborane-9

Expt- inert No.	M <sub>1</sub> , B <sub>5</sub> H <sub>9</sub> Used, mole	C <sub>2</sub> H <sub>4</sub> Pressure, p.s.i.g.	C <sub>2</sub> H <sub>4</sub> , mole	Molar Ratio		Bath Temp- ature, h. C	Composition of Product, %			Weight of Product, g.	M <sub>2</sub> , B <sub>5</sub> H <sub>9</sub> Recovered, mole	M <sub>3</sub> , B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub> Formed, mole	Boron Loss, %
				C <sub>2</sub> H <sub>4</sub> / B <sub>5</sub> H <sub>9</sub>	AlCl <sub>3</sub> / B <sub>5</sub> H <sub>9</sub>		B <sub>5</sub> H <sub>9</sub>	B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub>	Impurity				
9	0.0320	24	0.083	2.58	0.334	70°	74.2	24.2	1.6	2.10	0.0247	0.0056	5.3
4	0.0332	112	0.271	8.16	0.322	60°	85.9	12.6	1.5	2.07	0.0282	0.0029	6.3
3	0.0304	110	0.267	8.77	0.352	60°	72.9	20.1	7.1	2.11	0.0243	0.0046	4.9
2	0.0295	109	0.264	8.96	0.363	60°	78.8	19.9	1.4	1.95	0.0243	0.0043	3.1
1	0.0289	112	0.271	9.37	0.370	60°	87.3	10.7	2.0	1.82	0.0252	0.0021	5.5
10	0.0324	22.5	0.080	2.45	0.330	50°	50.2	49.6	0.2	2.24	0.0178	0.0122	7.4
11	0.0318	26	0.087	2.74	0.315	40°	53.8	46.1	0.0	2.275	0.0194	0.0115	2.8
12	0.0312	20	0.074	2.38	0.343	Room	48.6	50.9	0.5	2.257	0.0174	0.0126	3.8

$$\frac{M_1 - (M_2 + M_3)}{M_1} \times 100$$

/TABLE 3 .....



TABLE 3

Effect of Catalyst Ratio on the Ethylation of Pentaborane-9

Experiment No.	M <sub>1</sub> , B <sub>5</sub> H <sub>9</sub> Used, mole	C <sub>2</sub> H <sub>4</sub> Pressure, p.s.i.g.	C <sub>2</sub> H <sub>4</sub> , mole	Molar Ratio		Bath Temp., C	Time, h.	Composition of Product, %		Weight of Product, g.	M <sub>2</sub> , B <sub>5</sub> H <sub>9</sub> Recovered, mole	M <sub>3</sub> , B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub> Formed, mole	Boron Loss, %
				C <sub>2</sub> H <sub>4</sub> /B <sub>5</sub> H <sub>9</sub>	AlCl <sub>3</sub> /B <sub>5</sub> H <sub>9</sub>			B <sub>5</sub> H <sub>9</sub>	B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub> Impurity				
5	0.0329	105	0.256	7.78	0.965	60°	6	71.5	25.2	1.83	0.0207	0.0050	21.9
6	0.0332	30	0.096	2.90	0.959	60°	3	62.2	34.7	1.95	0.0192	0.0074	19.9
7	0.0336	33	0.102	3.03	0.950	60°	6	50.5	47.4	2.25	0.0180	0.0117	11.6
22	0.0325	34	0.1025	3.15	0.659	Room	69	48.5	50.3	1.99	0.0153	0.0110	19.1
20	0.0332	18	0.070	2.11	0.322	Room	65	87.4	12.6	2.17	0.0300	0.0030	0.6

$$\frac{M_1 - (M_2 + M_3)}{M_1} \times 100$$



TABLE 4

Effect of Ethylene Pressure on the Ethylation of Pentaborane-9

Experiment No.	M <sub>1</sub> , B <sub>5</sub> H <sub>9</sub> Used, mole	C <sub>2</sub> H <sub>4</sub> Pressure, p.s.i.g.	C <sub>2</sub> H <sub>4</sub> , mole	Molar Ratio		Bath Temperature, °C	Composition of Product, %			Weight of Product, g.	M <sub>2</sub> , B <sub>5</sub> H <sub>9</sub> Recovered, mole	M <sub>3</sub> , B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub> Formed, mole	Boron Loss, %
				C <sub>2</sub> H <sub>4</sub> /B <sub>5</sub> H <sub>9</sub>	AlCl <sub>3</sub> /B <sub>5</sub> H <sub>9</sub>		B <sub>5</sub> H <sub>9</sub>	B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub>	Impurity				
13	0.0321	100	0.245	7.64	0.333	Room	80.1	20.0	0.0	2.088	0.0265	0.0046	3.1
14	0.0322	50	0.138	4.30	0.332	Room	70.9	26.8	2.2	2.152	0.0242	0.0063	5.3
8	0.0343	28	0.091	2.66	0.312	60°	54.4	43.9	1.7	2.230	0.0192	0.0107	12.8
18	0.0350	20	0.074	2.12	0.306	Room	38.3	59.2	2.5	2.635	0.0160	0.0171	5.4
19	0.0327	15	0.064	1.94	0.327	Room	29.0	70.7	0.3	2.382	0.0109	0.0185	10.1
17	0.0329	10	0.053	1.61	0.325	Room	33.8	65.3	0.9	2.533	0.0135	0.0181	4.0
16	0.0331	5 (i)	0.042	1.27	0.323	Room	55.0	44.8	0.2	2.297	0.0200	0.0113	5.4
15	0.0323	5 (ii)	0.042	1.30	0.331	Room	23.4	71.8	4.8	2.370	0.0088	0.0187	14.9

$$\frac{M_1 - (M_2 + M_3)}{M_1} \times 100$$

/4.5 .....



#### 4.5 Effect of Ethylene Pressure

A steady increase in yield of ethyl pentaborane was observed in a series of experiments (Table 4) in which the initial pressures of ethylene were reduced by stages from 100 to 5 p.s.i.g. The relatively low yield (44.8 per cent) obtained in experiment 16 (21 hours) indicated that a long reaction time was necessary when the ethylene:pentaborane ratio approached unity.

The 2-stage reaction involved in experiment 15 gave a high yield of ethyl pentaborane but the product contained an undesirable quantity of impurity. The latter gave a smaller retention volume than pentaborane on the gas chromatogram (cf. Fig. 3).

#### 4.6 Consumption of Ethylene

In later experiments when low pressures of ethylene were used it was convenient to measure ethylene gas volumetrically before and after each experiment (Table 5, p.10). It is interesting to note the relatively high consumption of ethylene associated with a high catalyst ratio (experiment 22) and with a high ethylene pressure (experiment 23). The yield of 73.6 per cent recorded in experiment 24 is the highest obtained during the present investigation.

#### 4.7 Fractional Distillation of Pentaborane/Ethyl Pentaborane

Bulked reaction products (10.0 g.) containing pentaborane (28.7 per cent), ethyl pentaborane (70.9 per cent) and impurity (0.4 per cent) were fractionally distilled in the apparatus shown in Figure 4. The fractionating column was packed with stainless steel Dixon gauzes ( $\frac{1}{8} \times \frac{1}{8}$  inch; 100 B.S.S. mesh) and the receiver was cooled in solid-carbon-dioxide/acetone. A small positive pressure of dry nitrogen (ca. 780 mm.Hg) was maintained in the system throughout the distillation.

The results obtained by fractionating the mixture are presented in Table 6 (p.10) together with gas chromatographic analyses of the three fractions. It was found that over 80 per cent of the ethyl pentaborane could be obtained free from pentaborane and impurity.

Thermal decomposition occurred to a very slight extent during distillation as evidenced by the formation of a small quantity of ethane and the deposition of a brown film in the still.

#### 4.8 Hydrolysis

Although many of the physical properties of ethyl pentaborane have been measured (21) and some attention has been given to its thermal decomposition (22) no effort has been made to examine its behaviour on hydrolysis. As part of another investigation (23) the rates of hydrolysis of decaborane, ethyl decaborane and ethyl pentaborane were measured by treating known amounts of the boranes (ca. 0.1 g.) with dioxane (25 c.c.)/normal hydrochloric acid (5 c.c.) at 30°C.

/TABLE 5 .....



TABLE 5

Consumption of Ethylene During Alkylation

Experiment No.	M <sub>1</sub> , B <sub>5</sub> H <sub>9</sub> Used, mole	C <sub>2</sub> H <sub>4</sub> Pressure, p.s.i.g.	C <sub>2</sub> H <sub>4</sub> Used, mole	Molar Ratio		Temperature, °C	Time, h.	Composition of Product, %			Weight of Product, g.	M <sub>2</sub> , B <sub>5</sub> H <sub>9</sub> Recovered, mole	M <sub>3</sub> , B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub> Formed, mole	Boron Loss, %	C <sub>2</sub> H <sub>4</sub>	
				C <sub>2</sub> H <sub>4</sub> /B <sub>5</sub> H <sub>9</sub>	AlCl <sub>3</sub> /B <sub>5</sub> H <sub>9</sub>			B <sub>5</sub> H <sub>9</sub>	B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub>	Impurity					Recovered, mole	Consumed, mole
22	0.0325	34	0.1025	3.153	0.659	Room	69	48.5	50.3	1.2	1.990	0.0153	0.0110	19.1	0.0313	0.0712
23	0.0308	29	0.0937	3.040	0.347	Room	64	39.0	60.2	0.8	2.054	0.0127	0.0136	14.6	0.0360	0.0577
24	0.0321	5	0.0408	1.271	0.333	Room	114	25.5	73.6	0.9	2.406	0.0097	0.0194	9.3	0.0044	0.0364

/TABLE 6 .....

$$\frac{M_1 - (M_2 + M_3)}{M_1} \times 100$$

TABLE 6

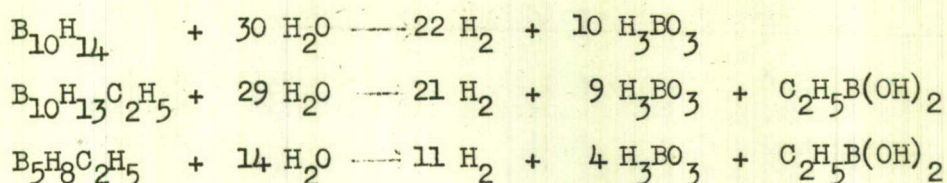
Fractional Distillation of Pentaborane/Ethyl Pentaborane

Fraction No.	Bath Temperature, °C	Internal Temperature, °C	Weight of Fraction, g.	Composition, %			Weight, g.		
				Impurity	B <sub>5</sub> H <sub>9</sub>	B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub>	Impurity	B <sub>5</sub> H <sub>9</sub>	B <sub>5</sub> H <sub>8</sub> C <sub>2</sub> H <sub>5</sub>
1	135 - 160	60 - 62	1.90	1.3	95.5	3.2	0.03	1.82	0.06
2	165 - 170	62 - 104	1.81	0.0	32.9	67.1	0.0	0.60	1.21
Residue			6.23	0.0	0.0	100.0	0.0	0.0	6.23
Total			9.94	-	-	-	0.03	2.42	7.50
Original Mixture			10.00	0.4	28.7	70.9	0.04	2.87	7.09

/Figure .....



Figure 5 illustrates the relative rates of decomposition calculated from the rates of evolution of hydrogen, assumed to be liberated according to the following equations:



The comparative instability of ethyl pentaborane was clearly demonstrated; hydrolysis was 97 per cent complete in 60 minutes.

## 5. DISCUSSION

### 5.1 Preparation

The following generalisations emerge from a study of the results in Tables 2 to 5.

- (i) High temperatures do not favour ethylation of pentaborane.
- (ii) Increasing the amount of catalyst causes high boron losses.
- (iii) High ethylene pressures give low yields of ethyl pentaborane at room temperature and at 60°C.

In view of the well-known reversibility of Friedel Crafts reactions it seems likely that high reaction temperatures may cause de-alkylation of ethyl pentaborane. High boron losses in the presence of increased amounts of catalyst may well be due to self-condensation of boron-containing compounds or to complex formation between these compounds and aluminium chloride. The adverse effect of high pressure may be due to increased interaction between ethylene and aluminium chloride.

The optimum conditions for ethyl pentaborane formation involve low pressures of ethylene, a small ratio of catalyst to pentaborane and reaction at ambient temperature. Under such conditions, and in a vessel which cannot be agitated or stirred, a long reaction time is required.

It is known that alkyl halides react rapidly with pentaborane in the presence of aluminium chloride and the reactions proceed rapidly at or below room temperature. Clearly, such reaction conditions should favour high yields of ethyl pentaborane although it has been shown during the present investigation that side-reactions may occur involving reduction of the alkyl halide to the corresponding hydrocarbon.

### 5.2 Purification

Separation of pentaborane/ethyl pentaborane mixtures by methods based on low-temperature distillation is known to be tedious (1). Preparative-scale gas chromatography is readily applicable to small quantities of such mixtures and has proved valuable in providing samples of ethyl pentaborane for elemental analysis (5). The present investigation shows that large scale purification may be successfully achieved by fractional distillation at atmospheric pressure, whereby impurity and pentaborane are removed. The residue which consists of pure ethyl pentaborane,

/in .....



in amount corresponding to more than 80 per cent of the quantity originally present in the mixture, may be readily transferred by subsequent vacuum distillation.

### 5.3 Comparison of Ethyl Pentaborane and Ethyl Decaborane

The choice of a particular organoborane as a possible high energy fuel depends not only upon its heat of combustion but also upon its ease of manufacture and purification and its physical and chemical properties.

Two important points established by the present work are that pentaborane may be converted to ethyl pentaborane in good yield, and that ethylation does not proceed beyond mono-substitution. On the other hand, ethyl decaborane readily undergoes further reaction to yield undesirable polyalkylated substances of low heating value.

Purification of ethyl pentaborane is relatively easy, too, compared with the distillation of ethyl decaborane (b.p. 217°C). Mixtures containing ethylated derivatives of decaborane can be distilled under high vacuum but complete separation of components is not possible (1).

However, consideration of the calculated heats of combustion of organoboranes (Table 7) (9) shows that, despite the advantage exhibited by pentaborane itself, ethyl and propyl derivatives have lower heating values than the corresponding compounds of decaborane.

TABLE 7

#### Heats of Combustion of Organoboranes

Borane	Heat of Combustion (to crystalline B <sub>2</sub> O <sub>3</sub> ), B.t.u./lb.			
	Unsubstituted	Methyl	Ethyl	Propyl
Pentaborane	29,400	27,200	25,900	25,000
Decaborane	28,500	27,300	26,700	26,000

Some of the more important physical properties of the lower alkyl derivatives of pentaborane and decaborane are compared in Table 8; methyl pentaborane is omitted because it is too volatile to be considered useful as a fuel. Limitations are imposed on the usefulness of ethyl pentaborane because of its high vapour pressure and low density.

/TABLE 8 .....



TABLE 8

Comparison of Ethyl Pentaborane, Methyl and Ethyl Decaborane

Property	Ethyl Pentaborane	Methyl Decaborane	Ethyl Decaborane
Vapour pressure, mm. Hg.	29/19.5°C (1)	Less than 1/25°C(1)	Less than 1/25°C(1)
Boiling point, °C	104	223 (1)	217 (1)
Melting point, °C	-85 (1)	-14 to -12(1)	-25 (1)
Density	0.68 (21)	0.80(Hef-4)(6)	0.80-0.82(Hef-3)(6)
Viscosity, centistokes	0.66/20°C (21)	9/25°C(Hef-4)(6)	9/25°C (Hef-3)(6)

The figures in parentheses are Bibliography references

Ethyl decaborane is more stable than ethyl pentaborane with respect to hydrolysis (see Section 4.8) and thermal decomposition. McDonald (20, 22, 24-26) examined the behaviour of various boranes and organoboranes on heating and, although the experiments were not always strictly comparable, the following order of thermal stability emerged: decaborane > ethyl decaborane > pentaborane > ethyl and propyl pentaborane.

In general it has been found that decaborane and its derivatives are more easily handled than pentaborane and alkyl pentaboranes. Pentaborane is spontaneously inflammable in air, as also are mixtures of pentaborane and ethyl pentaborane. By contrast decaborane and its derivatives do not appear to be affected by dry air and are attacked only slowly by atmospheric moisture.

Although ethyl pentaborane is more easily prepared and purified than ethyl decaborane, the latter is more attractive as a high energy fuel because of lower vapour pressure, higher heat of combustion, density, thermal and hydrolytic stability and the greater ease of handling of decaborane and its derivatives. These considerations are evidently well-known in the U.S.A., where boron fuels based on decaborane (HiCal-3, Hef-3 and Hef-4) are preferred to those derived from pentaborane (Hef-2) (6,27).

## 6. CONCLUSIONS

- 6.1 Ethyl pentaborane may be obtained in 74 per cent yield by the Friedel Crafts ethylation of pentaborane-9 with ethylene in the presence of aluminium chloride.
- 6.2 High yields of ethyl pentaborane are favoured by low ethylene pressure, a catalyst: pentaborane ratio of 1:3 and reaction at ambient temperature. Under these conditions, in an unstirred

/autoclave .....



autoclave, a long reaction time is necessary.

- 6.3 Over 80 per cent of the ethyl pentaborane in a typical reaction product can be separated from pentaborane and impurity by fractional distillation under a small positive pressure of nitrogen.
- 6.4 After 1 hour in a dioxane/hydrochloric acid medium at 30°C the relative extents of decomposition of ethyl decaborane, decaborane and ethyl pentaborane are 6.7, 9.7 and 97.0 per cent.
- 6.5 Consideration of the usefulness of ethyl pentaborane and ethyl decaborane as possible high energy fuels suggests that the former has certain advantages with regard to preparation and purification but the latter is to be preferred because of lower vapour pressure, higher heat of combustion, density, thermal and hydrolytic stability and, in general, because of the greater ease with which decaborane and its derivatives can be handled.

## 7. ACKNOWLEDGEMENTS

The authors are very grateful to Dr. R.L. Williams and Mr. N.J. Blay who performed many of the gas chromatographic analyses quoted herein. Thanks are also due to Dr. T.M. Walters for his advice during the course of the work and to Dr. A.J. Owen who supplied pentaborane-9.

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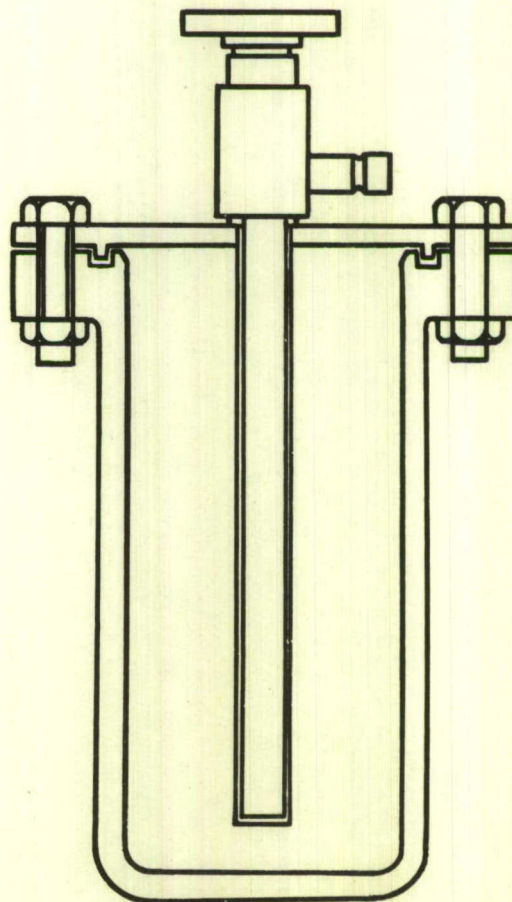
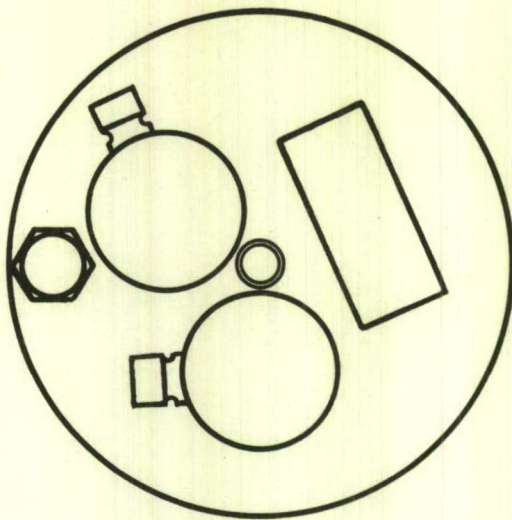


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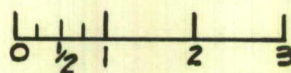
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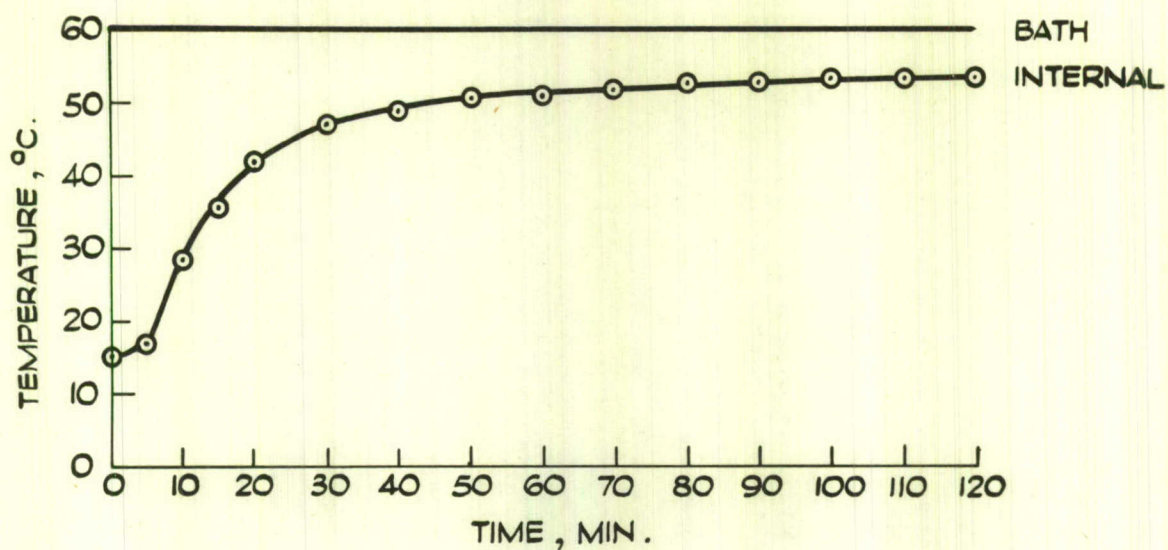
PENTABORANE/ETHYLENE REACTION AUTOCLAVE.

FIG. 1.

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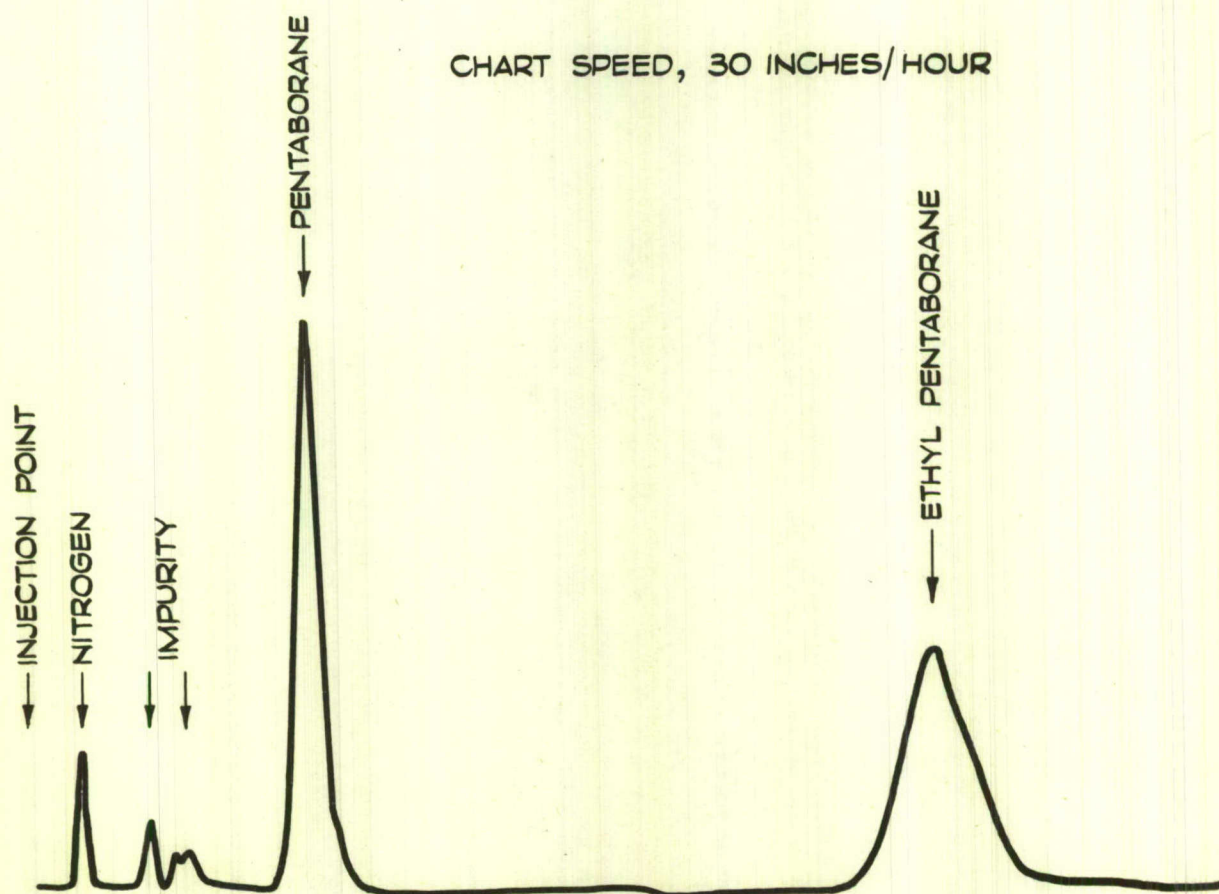


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CHANGE OF INTERNAL TEMPERATURE OF AUTOCLAVE  
WITH TIME.

FIG. 2.



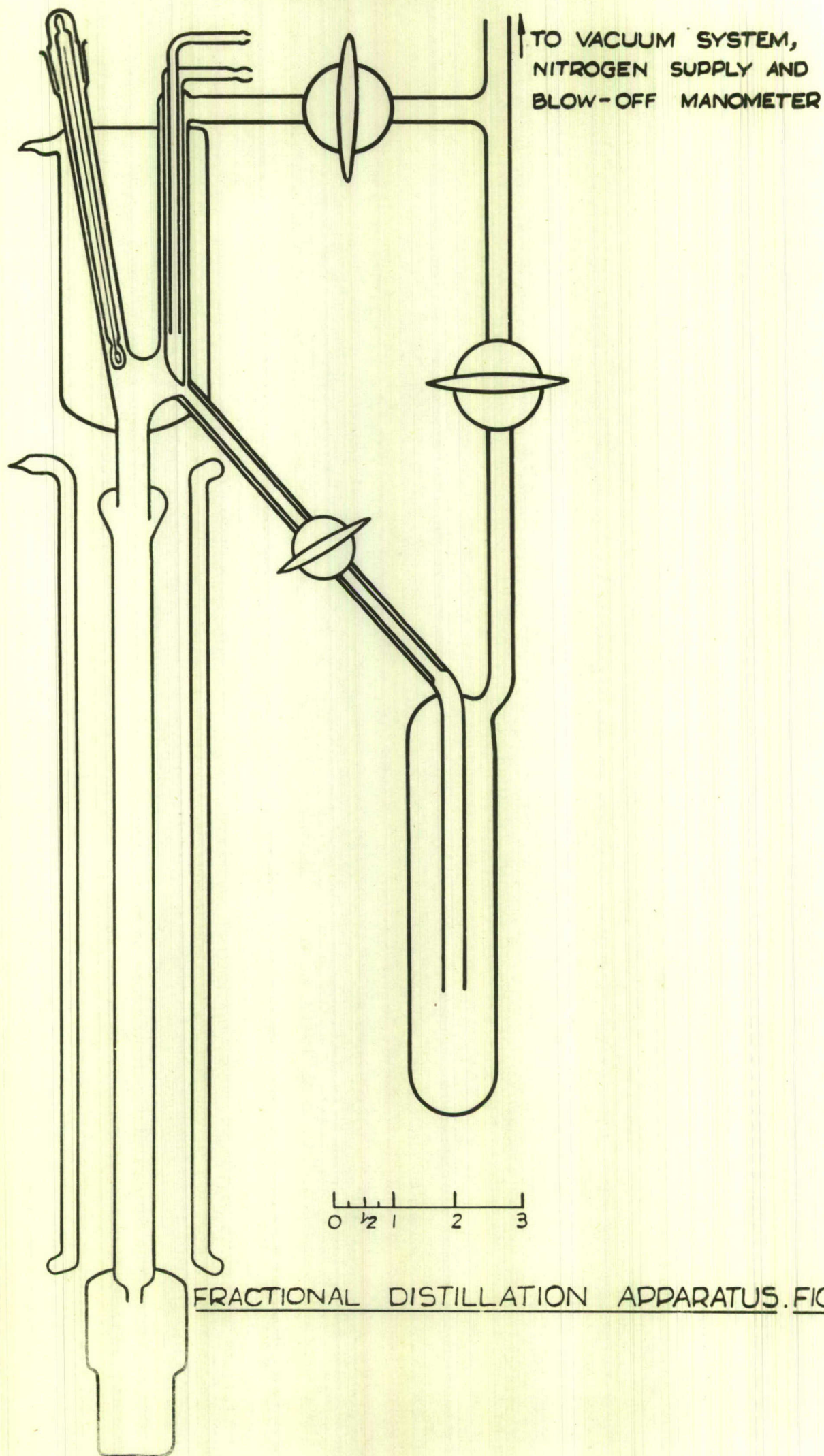
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FIG. 3.

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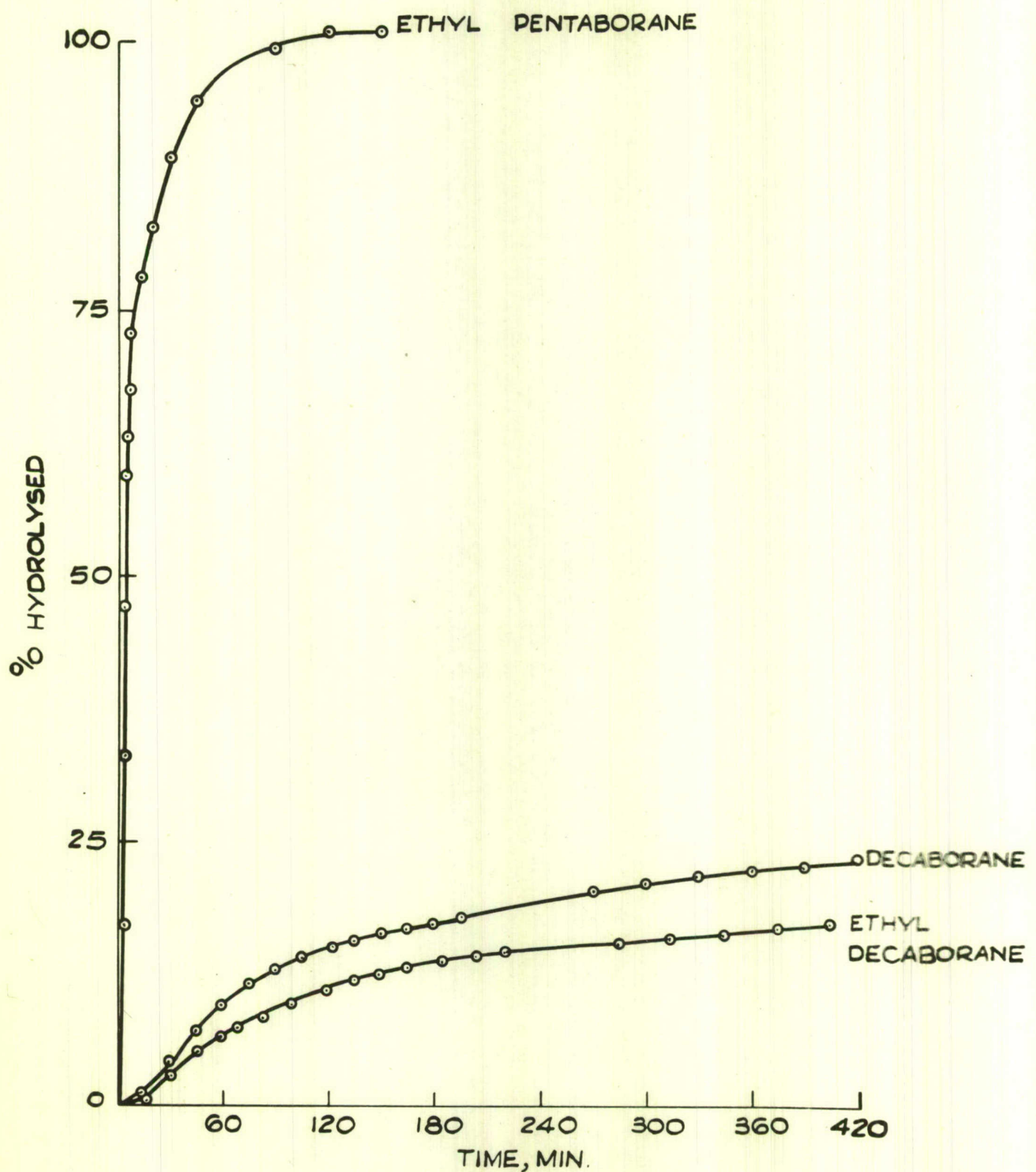


FRACTIONAL DISTILLATION APPARATUS. FIG. 4.

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HYDROLYSIS OF ALKYL BORANES IN DILUTE  
HYDROCHLORIC ACID/DIOXANE. FIG.5.

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I. Dunstan and J.V. Griffiths                      Jan., 1960

The known alkyl derivatives of pentaborane-9 are reviewed.

Optimum conditions for the preparation of ethyl pentaborane were determined by studying the Friedel Crafts reaction of pentaborane with ethylene/aluminium chloride. High yields were favoured by low ethylene pressure, a small ratio of catalyst to pentaborane, and reaction at ambient temperature.

Over 80 per cent of the ethyl pentaborane in a typical reaction product was recovered in a pure state by fractional distillation under a small positive nitrogen pressure.

Rates of hydrolysis of ethyl decaborane, decaborane and ethyl pentaborane were measured in a dioxane/hydrochloric acid medium; decomposition percentages after 1 hour at 30°C were 6.7, 9.7 and 97.0 respectively.

The preparation, purification and properties of ethyl pentaborane and ethyl decaborane are compared and discussed.  
15 pp., 5 fig., 8 tables

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